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14. ABSTRACT

Energetic materials of many different varieties (e.g., nitramines [RDX, HMX, CL20], high nitrogen content species [e.g., DAATO, tetrazines, tetazine N-oxides, furazans, tetrazoles] and others) are studies in order to explicate their detailed molecular decomposition dynamics kinetics, and mechanisms.This molecular level understanding is essential in order to determine their fundamental energy storage and release properties and behavior for fuels, explosives, and energy storage systems.The molecules are placed in the gas phase for isolation by matrix assisted

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Report Title

Electronic State Decomposition of Energetic Materials and Model Systems

ABSTRACT

Energetic materials of many different varieties (e.g., nitramines [RDX, HMX, CL20], high nitrogen content species [e.g., DAATO, tetrazines, tetazine N-oxides, furazans, tetrazoles] and others) are studies in order to explicate their detailed molecular decomposition dynamics kinetics, and mechanisms.This molecular level understanding is essential in order to determine their fundamental energy storage and release properties and behavior for fuels, explosives, and energy storage systems.The molecules are placed in the gas phase for isolation by matrix assisted laser desorption, cooled in a supersonic expansion, and excited for ignition by single photon absorption. Nano- and femto-second spectroscopy are carried out in the energetic and model systems to elucidate and compare their behavior.Theoretical studies are carried out to understand the electronic potential energy surfaces and their interactions for the decomposition mechanisms. These states interact at conical intersections, which control the energy release mechanisms. New compounds can be suggested to enhance or control energetic behavior.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

A. Bhattacharya, Y. Q. Guo, and E. R. Bernstein, "Nonadiabatic Chemistry of Energetic Molecules," Acc. Chem. Res. Submitted.
A. Bhattacharya, J. -W. Shin, K. J. Clawson, and E. R. Bernstein, "Conformation Specific and Charge Directed Reactivity of Radical Cation Intermediates of a-Substituted (Amino, Hydroxy, and Keto) Bioactive Carboxylic Acids," Phys. Chem. Chem. Phys. 12, 9700 (2010).
F. Dong, S. Heinbuch, Y. Xie, J. J. Rocca, and E. R. Bernstein, "Experimental and Theoretical Studies of Neutral AlmCn and AlmCnHx Clusters," Phys. Chem. Chem. Phys. 12, 2569 (2010).
A. Bhattacharya, Y. Q. Guo, and E. R. Bernstein, "Unimolecular Decomposition of Tetrazine-N-Oxide Based High Nitrogen Content Energetic Materials from Excited Electronic States," J. Chem. Phys. 131, 194304 (2009).
A. Bhattacharya, Y. Q. Guo, and E. R. Bernstein, "Experimental and Theoretical Exploration of the Initial Steps in the Decomposition of a Model Nitramine Energetic Material: Dimethylnitramine," J. Phys. Chem. A 113, 811 (2009).
Y. Q. Guo, A. Bhattacharya, and E. R. Bernstein, "Photodissociation Dynamics of Nitromethane at 226 nm and 271 nm at both Nanosecond and Femtosecond Temporal Scales," J. Phys. Chem. A 113, 85 (2009).
Y. Q. Guo, A. Bhattacharya and E. R. Bernstein, "Excited Electronic State Decomposition of Furazan Based Energetic Materials: 3,3?-Diamino-4,4?-Azoxyfurazan (DAAF) and its Model Systems, Diaminofurazan (DAF) and Furazan," J. Chem. Phys. 128, 034303 (2008).
Y. Q. Guo, M. Greenfield, A. Bhattacharya, and E. R. Bernstein, "On the Excited Electronic State Dissociation of Nitramine Energetic Materials and Model Systems," J. Chem. Phys. 127, 154307 (2007)

Number of Papers published in peer-reviewed journals: 7.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

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Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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(d) Manuscripts

A. Bhattacharya and E. R. Bernstein, "Influence of Turn (or Fold) and Local Charge in the Fragmentation of Peptide Analogue Molecule, NH2-Gly-COCH3 Following Single Photon Ionization at 10.5 eV," In preparation.
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A. Bhattacharya and E. R. Bernstein, "Excited Electronic State Decomposition of Gas Phase RDX: An ONIOM-CASSCF Study," In preparation.
Y. Q. Guo, A. Bhattacharya, and E. R. Bernstein, "Excited Electronic State Decomposition of s-Tetrazine and its Energetic Derivatives," In preparation.

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Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED
M. Greenfield	0.00
A.	1.00
FTE Equivalent:	**1.00**
Total Number:	**2**

Names of Post Doctorates

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Z.J. Yu	1.00
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J J Rocca	0.00	No
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Total Number:	**2**	

Names of Under Graduate students supported

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FTE Equivalent:	**0.00**
Total Number:	**1**

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period:	0.00
The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:.....	0.00
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ARO Final Report

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The basic idea behind this research program is that energetic materials are excited electronically ($S_o \rightarrow S_m$) upon the shock, spark, plasma, laser, etc. ignition event, and that these excited electronic states are the initiators of the decomposition process in which an energetic molecule releases its energy. The initial step in this process releases small radical molecules, such as NO, N_2, NH_3, etc., and this process occurs rapidly, on the order of 100 fs. The mechanisms for this release of energy involve radiationless and diabatic (non-adiabatic) electronic state interactions and transition involving conical intersections between potential energy surfaces. Thus a chain of events occurs, such as $S_m \rightarrow S_{m-1} \rightarrow \cdots \rightarrow S_o \rightarrow$ fragments: little rotational energy is imprinted to the fragments. The difference between an energetic and a model, non-energetic species (e.g., RDX vs DMNA, tetrazine vs ACTO, DAATO and others) can be understood based on S_m (model) vs S_o (energetic) molecular decomposition, and the internal excitation (especially rotational) of the initial products of decomposition. One can understand energetic materials and how to structure them based on the behavior of their adiabatic potential energy surfaces and their mutual interactions.

The fundamental goals of the program are to understand the detailed molecular mechanisms for decomposition of energetic materials (that is, the release of their stored energy), and to apply this knowledge to the creation and synthesis of improved and new energetic species. Achieving these goals will enable the

production of new specific systems for better and more stable fuels, explosives, and mobile energy sources.

The specific systems we have studied over the grant period are given below, with some detail of particular results.

1.Decomposition of tetrazine-N-oxide based high nitrogen content energetic materials from excited electronic states

Unimolecular excited electronic state decomposition of novel high nitrogen content energetic molecules, such as 3,3'-azobis(6-amino-1,2,4,5-tetrazine)-mixed N-oxides (DAATO3.5), 3-amino-6-chloro-1,2,4,5-tetrazine-2,4-dioxide (ACTO), and 3,6-diamino-1,2,4,5-tetrazine1,4-dioxde (DATO), is investigated. Although these molecules are based on N-oxides of a tetrazine aromatic heterocyclic ring, their decomposition behavior distinctly differs from that of bare tetrazine, in which N_2 and HCN are produced as decomposition products through a concerted dissociation mechanism. NO is observed to be an initial decomposition product from all tetrazine-N-oxide based molecules following their excitation to low lying excited electronic states. The NO product from $DAATO_{3.5}$ and ACTO is rotationally cold (20 K) and vibrationally hot (1200 K), while the NO product from DATO is rotationally hot (50 K) and vibrationally cold [only the (0–0)vibronic transition of NO is observed]. $DAATO_{3.5}$ and ACTO primarily differ from DATO with regard to molecular structure, by the relative position of oxygen atom attachment to the tetrazine ring. Therefore, the relative position of oxygen in tetrazine-N-oxides is proposed to play an important role in their energetic behavior. N_2O is ruled out as an intermediate precursor of the NO product observed from all three molecules. Theoretical calculations at CASMP2/CASSCF level of theory predict a ring contraction mechanism for generation of the initial NO product from these molecules. The ring contraction occurs through a $(S_1/S_0)_{CI}$ conical intersection.

2. Decomposition of a Model Nitramine Energetic Material: Dimethylnitramine

Decomposition of dimethylnitramine (DMNA, (CH3)2NNO2) has been studied extensively over the past decades. Although several different mechanisms have been proposed for the initial decomposition of DMNA, the dominant decomposition channel is still far from fully understood. In this effort, nanosecond laser, energy resolved spectroscopy and complete active space self-consistent field (CASSCF) calculations are employed. The parent DMNA molecule is electronically excited using two different UV excitation wavelengths, 226 and 193 nm, to initiate the decomposition process. The NO molecule is observed as a major decomposition product with relatively hot (120 K) rotational and cold vibrational distributions by both time-of-flight mass spectrometry and laser induced fluorescence spectroscopy. On the basis of the experimental observations, a nitro-nitrite isomerization mechanism is predicted to be the major channel of decomposition of DMNA in the excited electronic state with a minor contribution from the HONO elimination mechanism. The branching ratio between nitro-nitrite isomerization and HONO elimination channels is estimated to be approximately 1:0.04. CASSCF calculations

show that surface crossing (conical intersection) between upper and lower electronic states along the nitro-nitrite isomerization reaction coordinate play an important role in the overall decomposition of DMNA. Presence of such a $(S_2/S_1)_{CI}$ conical intersection in the nitro-nitrite isomerization reaction coordinate provides a direct nonadiabatic decomposition pathway from the Franck-Condon point of the S_2 surface, which is experimentally accessed by 226 nm photoexcitation. This excited state isomerization takes place through a loose geometry for which the NO_2 moiety interacts with the $(CH_3)_2N$ moiety from a long distance (~2.8 Å); however, in the ground electronic state, a similar $(S_1/S_0)_{CI}$ conical intersection in this nitro-nitrite isomerization reaction coordinate hinders the isomerization exit channel, rendering NO_2 elimination as the major thermal decomposition channel of DMNA.

3. Decomposition of furazan based energetic materials: 3,3'-diamino-4,4'-azoxyfurazan and its model systems, diaminofurazan and furazan

These are the first experimental and theoretical studies of gas phase excited electronic state decomposition of a furazan based, high nitrogen content energetic material, 3,3'-diamino¬4,4'-azoxyfurazan (DAAF), and its model systems, diaminofurazan (DAF) and furazan ($C_2H_2N_2O$). The NO molecule is observed as an initial decomposition product from DAAF and its model systems at three UV excitation wavelengths (226, 236, and 248 nm) with a pulse duration of 8 ns. A unique excitation wavelength independent dissociation channel is observed for DAAF, which generates the NO product with a rotationally cold (20 K)and a vibrationally hot (1265 K) distribution. On the contrary, excitation wavelength dependent dissociation channels are observed for the model systems, which generate the NO product with both rotationally cold and hot distributions depending on the excitation wavelengths. Potential energy surface calculations at the CASSCF level of theory illustrate. That two conical intersections between the excited and ground electronic states are involved in two different excitation wavelength dependent dissociation channels for the model systems. Femtosecond pump-probe experiments at 226 nm reveal that the NO molecule is still the main observed decomposition product from the materials of interest and that the formation dynamics of the NO product is faster than 180 fs.

4.Ultrafast dissociation dynamics of excited electronic state HMX and RDX via femtosecond laser pump–probe techniques

Femtosecond laser pump–probe techniques are employed to investigate the mechanisms and dynamics of the photodissociation of HMX and RDX from their excited electronic states at three wavelengths (230 nm, 228 nm, and 226 nm). The only observed product is the NO molecule. Parent HMX and RDX ions are not observed. The NO molecule has a resonant $A^2 \sum \leftarrow x^2 \prod (0, 0)$ transition at 226 nm and off-resonance two-photon absorption at 228 nm and 230 nm. Pump–probe transients of the NO product at both off-resonance and resonance absorption wavelengths indicate the decomposition dynamics of HMX and RDX falls into the timescale of our laser pulse duration (180 fs).

5.Decomposition of s-tetrazine and its energetic derivatives

Excited electronic state decomposition of s-tetrazine and its energetic derivatives, such as 3-amino-6-chloro-1, 2, 4, 5-tetrazine-2,4-dioxide (ACTO), and 3,3′′-azobis (6-amino-1,2,4,5-tetrazine)-mixed N-oxides ($DAATO_{3.5}$), is investigated through laser excitation and resonance enhanced multi photon ionization (REMPI) techniques. As a concerted triple dissociation product from excited state decomposition of s-tetrazine, N_2 molecule is detected with a cold rotational distribution (20 K) via its two photon resonance absorption transitions [$a''\ ^1\Sigma_g^+$ (v′ = o) ← $X\ ^1\Sigma_g^+$ (v″ = o)] at 202 nm. Similar concerted triple dissociation product N2O is not observed from excited state decomposition of ACTO and $DAATO_{3.5}$; instead, NO molecule is observed as an initial decomposition product from these two derivatives. The NO products from ACTO and $DAATO_{3.5}$ exhibit similar cold rotational (20 K) and hot vibrational (1200 K) distributions. N_2O is ruled out as an intermediate precursor of the NO product observed from these two s-tetrazine derivatives. Theoretical calculation at the CASMP2/CASSCF level of theory predicts a concerted triple dissociation mechanism for the N_2 product from s-tetrazine, and a ring contraction mechanism for the NO product from the energetic s-tetrazine derivatives. The substituents on the tetrazine ring change the characteristics of the potential energy surfaces of the derivatives; this leads to a completely different decomposition pathway from s-tetrazine itself. Moreover, as an apparently potential decomposition product from high nitrogen content energetic materials, the N_2 molecule is ruled out as an initial product from excited state decompositions of these materials.

6. Decomposition of nitramine energetic materials and model systems.

In order to elucidate the difference between nitramine energetic materials, such as RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane), and CL-20 (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane), and their nonenergetic model systems, including 1,4-dinitropiperazine, nitropiperidine, nitropyrrolidine, and dimethylnitramine, both nanosecond mass resolved excitation spectroscopy and femtosecond pump-probe spectroscopy in the UV spectral region have been employed to investigate the mechanisms and dynamics of the excited electronic state photodissociation of these materials. The NO molecule is an initial decomposition product of all systems. The NO molecule from the decomposition of energetic materials displays cold rotational and hot vibrational spectral structures. Conversely, the NO molecule from the decomposition of model systems shows relatively hot rotational and cold vibrational spectra. In addition, the intensity of the NO ion signal from energetic materials is proportional to the number of nitramine functional groups in the molecule. Based upon experimental observations and theoretical calculations of the potential energy surface for these systems, we suggest that energetic materials dissociate from ground electronic states after internal conversion from their first excited states, and model systems dissociate from their first excited states. In both

cases a nitro-nitrite isomerization is suggested to be part of the decomposition mechanism. Parent ions of dimethylnitramine and nitropyrrolidine are observed in femtosecond experiments. All the other molecules generate NO as a decomposition product even in the femtosecond time regime. The dynamics of the formation of the NO product is faster than 180 fs, which is equivalent to the time duration of our laser pulse.

7. Nonadiabatic Reaction of Energetic Molecules

Energetic materials are systems that store a large amount of chemical energy that can be readily converted into mechanical energy via decomposition. Excited electronic state decomposition of energetic materials can be initiated by a number of different ignition processes, such as sparks, shocks, heat, or arcs: experimentally, excited electronic state decomposition has been proved to play an essential role in the energy conversion process. In order to understand the mechanisms for the decomposition of energetic materials from excited electronic states fully, investigation and analysis of the specific topography of the excited electronic potential energy surfaces (PESs) of these molecules are necessary. Conical intersections (CIs), which create a funnel-like topography of PESs due to the crossing of multidimensional electronic PESs, have been firmly established to be a controlling factor in the excited electronic state decomposition of polyatomic molecules. A decomposition process involving CIs is an electronically nonadiabatic mechanism, because of the involvement of more than one PES. Based on our experimental observations and theoretical calculations, we find that nonadiabatic reaction through CIs dominates the initial decomposition process of energetic materials from excited electronic states. Although the nonadiabatic behavior of some polyatomic molecules has been well studied, the role of nonadiabatic reactions in the decomposition of excited electronic state energetic molecules has not been well investigated. Nonadiabatic unimolecular chemistry of energetic materials through CIs, supports the essential role of CI in the determination of decomposition pathways of these energetic systems. Both nanosecond energy resolved, and femtosecond time resolved, spectroscopic techniques are utilized to determine experimentally the decomposition mechanism and dynamics of energetic species. Subsequently, multiconfigurational methodologies (such as, CASSCF, CASMP2) are employed to model nonadiabatic molecular processes of energetic molecules. Synergism between experiment and theory establishes a coherent description of the nonadiabatic reactivity of energetic materials at a molecular level. A number of model systems, which have similar molecular structures to those of the energetic systems, but are themselves non-energetic, are first studied in detail to assist in understanding the nonadiabatic behavior of a specific moiety in an energetic system. Then, the decomposition mechanisms for more complex energetic systems are studied and compared with those of their model systems. Our results for the systems of interest confirm that the existence of CIs and the energy barriers for accessing them on the PESs of interest control the nonadiabatic behavior of the decomposition process. The detailed nature of the PESs and their CIs consequently

differentiate the energetic systems from model systems. Energy barriers to the chemically relevant low-lying CI of a molecule are determining factors for that molecule being more or less "energetic".

8. Photodissociation Dynamics of Nitromethane at 226 and 271 nm at Both Nanosecond and Femtosecond Time Scales

Photodissociation of nitromethane has been investigated for decades both theoretically and experimentally; however, as a whole picture, the dissociation dynamics for nitromethane are still not clear, although many different mechanisms have been proposed. To make a complete interpretation of these different mechanisms, photolysis of nitromethane at 226 and 271 nm under both collisional and collisionless conditions is investigated at nanosecond and femtosecond time scales. These two laser wavelengths correspond to the $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow$ m excitations of nitromethane, respectively. In nanosecond 226 nm ($\pi^* \leftarrow \pi$) photolysis experiments, CH_3 and NO radicals are observed as major products employing resonance enhanced multiphoton ionization techniques and time-of-flight mass spectrometry. Additionally, OH and CH_3O radicals are weakly observed as dissociation products employing laser induced fluorescence spectroscopy; the CH_3O product is only observed under collisional conditions. In femtosecond 226 nm experiments, CH_3, NO_2, and NO products are observed. These results confirm that rupture of C-N bond should be the main primary process for the photolysis of nitromethane after the $\pi^* \leftarrow \pi$ excitation at 226 nm, and the NO_2 molecule should be the precursor of the observed NO product. Formation of the CH_3O radical after the recombination of CH_3 and NO_2 species under collisional conditions rules out a nitro-nitrite isomerization mechanism for the generation of CH_3O and NO from $\pi^* \leftarrow \pi$ CH_3NO_2. The OH radical formation for $\pi^* \leftarrow \pi$ CH_3NO_2 should be a minor dissociation channel because of the weak OH signal in both nanosecond and femtosecond (nonobservable) experiments. Single color femtosecond pump-probe experiments at 226 nm are also employed to monitor the dynamics of the dissociation of nitromethane after the $\pi^* \leftarrow \pi$ excitation. Because of the ultrafast dynamics of product formation at 226 nm, the pump-probe transients for the three dissociation products are measured as an autocorrelation of the laser pulse, indicating the dissociation of nitromethane in the $\pi^* \leftarrow \pi$ excited state is faster than the laser pulse duration (180 fs). In nanosecond 271 nm ($\pi^* \leftarrow$ n) photolysis experiments, pump-probe experiments are performed to detect potential dissociation products, such as CH_3, NO_2, CH_3O, and OH; however, none of them are observed. In femtosecond 271 nm laser experiments, the nitromethane parent ion is observed with major intensity, together with CH_3, NO_2, and NO fragment ions with only minor intensities. Pump-probe transients for both nitromethane parent and fragment ions at 271 nm excitation and 406.5 nm ionization display a fast exponential decay with a constant time of 36 fs, which we suggest to be the lifetime of the excited $n\pi^*$ state of nitromethane. Combined with the 271 nm nanosecond pump-probe experiments, in which none of the CH_3, NO_2, CH_3O, or OH fragments is observed, we suggest that all the fragment ions generated in 271 nm femtosecond

laser experiments are derived from the parent ion, and dissociation of nitromethane from the $n\pi^*$ excited electronic state does not occur in a supersonic molecular beam under collisionless conditions.

List of Publications:

A. Bhattacharya and E. R. Bernstein, "Influence of Turn (or Fold) and Local Charge in the Fragmentation of Peptide Analogue Molecule, NH_2-Gly-$COCH_3$ Following Single Photon Ionization at 10.5 eV," In preparation.

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A. Bhattacharya, Y. Q. Guo, and E. R. Bernstein, "Nonadiabatic Chemistry of Energetic Molecules," Acc. Chem. Res. Submitted.

A. Bhattacharya, J. -W. Shin, K. J. Clawson, and E. R. Bernstein, "Conformation Specific and Charge Directed Reactivity of Radical Cation Intermediates of a-Substituted (Amino, Hydroxy, and Keto) Bioactive Carboxylic Acids," Phys. Chem. Chem. Phys. 12, 9700 (2010).

F. Dong, S. Heinbuch, Y. Xie, J. J. Rocca, and E. R. Bernstein, "Experimental and Theoretical Studies of Neutral Al_mC_n and $Al_mC_nH_x$ Clusters," Phys. Chem. Chem. Phys. 12, 2569 (2010).

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